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Evaluation of Photovac 10S50 Portable Photoionization Gas Chromatograph for Analysis of Toxic Organic Pollutants in Ambient Air

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U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Methods Development and Analysis Division
Research Triangle Park, N.C.

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by

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16. ABSTRACT

Analysis of vapor phase organic compounds in ambient air is usually done by gas chromatography using a mass spectrometer as detector (GC/MS). The principal advantage of GC/MS is its selectivity and range of applicability, and its principal disadvantage is its relatively high detection limit. Preconcentration of analytes is required for GC/MS because this analytical system cannot tolerate large quantities of oxygen and water and because mass spectrometers are not sufficiently sensitive to detect ambient levels of analytes in samples small enough to be chromatographed. Oxygen destroys chromatographic columns and mass spectrometer filaments and detectors. Water, present at about ten thousand times the concentration of most pollutants, may swamp an analytical system which can detect it. Because of this, atmospheric organic vapors which are analyzed by GC/MS must first be separated from the air matrix by preconcentration. Unfortunately, preconcentration produces many errors. Efficiency of pollutant collection and delivery to the GC/MS is low and variable for many compounds, and numerous artifacts are formed (1). Therefore preconcentration/GC/MS analysis of organic vapors in ambient air is at best a semiquantitative method which is expensive and labor-intensive. However, because of its effectiveness in qualitative analysis it is likely to remain virtually indispensable in the foreseeable future.

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FOREWORD

Monitoring research efforts are intended to anticipate environmental problems, to support regulatory actions by developing an understanding of processes which affect the ecology and human health, to provide means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology for air, implementation of agency-wide quality assurance programs for air pollution measurement, and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Analysis of organic compounds in the atmosphere is a difficult task which requires a variety of analytical techniques to ensure that identification and quantitation are valid. The environmental analyst needs methods which are precise, accurate, and easy to use. This study is concerned with the evaluation of a portable chromatograph equipped with a photoionization detector which is sensitive enough to detect several classes of pollutants at ambient levels without preconcentration. Its use in conjunction with existing methods may greatly improve the ability of the analyst to produce valid results.

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ABSTRACT

The objective of this study was to evaluate the Photovac 10S50 portable photoionization gas chromatograph as a monitor for fourteen selected toxic organic vapors in ambient air. These included benzene, toluene, bromo- and chloro-benzene, o-xylene, and nine halo-methanes, ethanes, and ethylenes. Such analyses have usually been done by gas chromatography using a mass spectrometer as detector (GC/MS). This has required preconcentration of analytes because the sensitivity of GC/MS is inadequate for ambient concentrations and the instrumentation is intolerant of oxygen. This procedure is inefficient in collection and delivery of analytes to the GC/MS system and limits GC/MS analysis of organic vapors in air to being a semiquantitative method which may produce misleading results. A portable chromatograph with a detector sensitive enough to detect pollutants without preconcentration could avoid these shortcomings and supplement or complement data obtained by preconcentration/GC/MS.

The Photovac 10S50 is a truly portable gas chromatograph which can be operated on battery power. It has dimensions of 46 X 16 X 34 centimeters (18.25 X 6.25 X 13.25 inches), weighs 11.8 kilograms (26 pounds), and includes a sampling pump, a column compartment, a 10.6 electron volt photoionization detector, and a microcomputer with printer-plotter. It can be operated either manually or in automatic sampling mode. Ultra zero air is used as carrier gas. A benzene detection limit of 0.1 parts per billion by volume is claimed, as well as the ability to detect at ambient concentrations many hazardous pollutants in air. Calibration and operation of the instrument are described in this report.

An extrapolated benzene detection limit of 95 femtograms was found. This was equivalent to 0.03 parts per billion by volume at 25 C. Response to benzene was linear over a range from the detection limit to 750 parts per billion. Field sampling was carried out near Research Triangle Park, North Carolina. Apparent ambient levels of benzene and toluene up to 17 parts per billion by volume were observed. Trichloroethylene and 1,1,1-trichloroethane also apparently were present. Installation of a fused-silica capillary column and modification of the sample loop to minimize dead volume resulted in improved resolution at the cost of a slight increase in retention times. The unit generally performed satisfactorily and lived up to most of the manufacturer's claims. It actually is portable and meets the claimed detection limit for benzene of 0.1 parts per billion by volume. It also can detect chloroethylenes at similar concentrations and chloromethanes and chloroethanes at 10- to 100-fold higher concentrations. Reliable unattended operation will require improved calibrant peak identification.

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SECTION 1

INTRODUCTION

Analysis of vapor phase organic compounds in ambient air is usually done by gas chromatography using a mass spectrometer as detector (GC/MS). The principal advantage of GC/MS is its selectivity and range of applicability, and its principal disadvantage is its relatively high detection limit. Preconcentration of analytes is required for GC/MS because this analytical system cannot tolerate large quantities of oxygen and water and because mass spectrometers are not sufficiently sensitive to detect ambient levels of analytes in samples small enough to be chromatographed. Oxygen destroys chromatographic columns and mass spectrometer filaments and detectors. Water, present at about ten thousand times the concentration of most pollutants, may swamp an analytical system which can detect it. Because of this, atmospheric organic vapors which are analyzed by GC/MS must first be separated from the air matrix by preconcentration. Unfortunately, preconcentration produces many errors. Efficiency of pollutant collection and delivery to the GC/MS is low and variable for many compounds, and numerous artifacts are formed (1). Therefore preconcentration/GC/MS analysis of organic vapors in ambient air is at best a semiquantitative method which is expensive and labor-intensive. However, because of its effectiveness in qualitative analysis it is likely to remain virtually indispensable in the foreseeable future.

Analyzing pollutants directly without separating them from air might avoid these problems, but to detect one part per billion by volume of benzene in one milliliter of air would require a three picogram detection capability. An analytical method based upon completely different approaches to sampling and detection of toxic organic pollutants could prove very useful, especially if it supplied data which has not been spoiled by gross sampling errors. Photoionization gas chromatography is capable of detecting many toxic organic pollutants without preconcentration. It is less selective than GC/MS because only retention times are used for identification, but since it does not use preconcentration, it avoids the inherent sampling errors. Because in field operation the samples are extremely small compared to the capacity of the column, and because the instrument is frequently recalibrated, accuracy of retention times is optimized. If a peak appears within the "window" of a certain compound, it can be either that compound or another compound of similar retention time. Positive identification is not established, but it is not possible that the "identified" compound can actually be present in a concentration larger than indicated by the peak which appears in its retention window unless there is some negative interference. Therefore the resulting data can generally be taken as credible estimates of upper limits of true concentrations.

The Photovac 10S50 is a portable gas chromatograph with a highly sensitive detector. It is primarily designed for industrial hygiene analysis of organic compounds. It is self contained, mounted in an aluminum case with internal electric power and carrier gas supplies. The unit measures 46 X 16 X 34 centimeters (18.25 X 6.25 X 13.25 inches) and weighs 11.8 kilograms (26 pounds). It is equipped with a microcomputer which controls sampling and analysis and processes data, and it has a built-in printer-plotter. Calibration gas can be delivered from an aerosol can mounted on the control panel inside the case. It possesses significant advantages over conventional gas chromatographs:

a. It is portable.
b. Its detector is sensitive enough to respond to ambient background levels of several toxic organic compounds without preconcentration (benzene, toluene, and the chloroethylenes, for example). It could be used as-is to screen for these compounds in ambient air or near hazardous waste sites. It also could be a valuable supplement or complement to GC/MS analysis.
c. Analyte concentrations are far below levels which could overload the column and lead to tailing or distortion of peaks.
d. It is tolerant of oxygen, so that separation of analytes from air is unnecessary.
e. It is blind to water.
f. It can be transported without special preparation.

There are also some disadvantages:

(a) Photoionization detectors are not as specific as mass spectrometers. "Identification" of a compound by photoionization gas chromatography is evidence, but not proof, of its presence.
(b) Because the column is exposed to large quantities of air, it must be operated at ambient or only slightly elevated temperatures. This reduces the quality of chromatographic resolution and limits analytes to compounds which have high vapor pressures at ambient temperatures.

In this study the Photovac 10S50 was evaluated for direct detection of fourteen organic pollutants commonly found in ambient air:

benzene	dichloromethane
toluene	trichloromethane
o-xylene	tetrachloromethane
chlorobenzene	1,2-dichloroethane
bromobenzene	1,2-dibromoethane
trichloroethylene	1,1,1-trichloroethane
tetrachloroethylene	1,1-dichloroethylene

Retention times were determined on a 0.125 inch X 4.5 foot, 5% SE-30 on 100/120 mesh Chromosorb G column which was supplied with the instrument and on a 0.53 millimeter X 25 meter fused-silica capillary column coated with a 5 micrometer chemically bonded layer of methyl silicone. The detection limit for benzene was determined by statistical analysis of a linear calibration plot. Linearity of response for benzene, toluene, and chlorobenzene was checked. Single-point calibration of the unit for each

compound was performed using standards prepared by static dilution of headspace vapors. Limited field evaluation was carried out in Research Triangle Park, North Carolina.

A detailed description of the Photovac 10S50, including the manufacturer's recommended operating procedures, is given in Section 3. Evaluation of the instrument is described in Section 4.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The Photovac 10S50 is capable as-is of monitoring, under operator supervision, ambient background levels of benzene, volatile substituted benzenes, and haloethylenes. Since it is easily capable of detecting part per million or lower levels of these compounds, it could be very useful for monitoring volatile effluents from hazardous waste sites, if used outdoors at 20 to 38 C (68 to 100 F) or for survey studies of indoor and ambient air. Since it operates without preconcentration, the results should not be subject to preconcentration artifacts. Because the calibration procedure reliably divides the chromatogram into "windows" in which each compound must appear if it appears at all, it can provide estimates of the upper limits of the concentrations of tentatively identified pollutants, regardless whether those identifications actually are correct. The Photovac 10S50 is a truly portable, self-contained instrument, and it generally performs as claimed by the manufacturer. However, some problems were encountered during the evaluation, and they are described herein.

National Bureau of Standards Standard Reference Material (NBS SRM) No. 1805 (0.254 parts per million benzene in nitrogen) was used to perform a calibration and to determine the detection limit for benzene. A plot of quantity (picograms) vs. response (millivolt*second) was linear over a range of 1.6 to 400 picograms with a correlation coefficient of 0.999. Linear response to benzene was observed over a wider range, from the detection limit to 750 parts per billion by volume with a correlation coefficient of 0.998. An extrapolated detection limit of 95 femtograms of benzene was calculated by dividing twice the standard deviation of the baseline by the slope. This corresponds to an atmospheric concentration of 30 parts per trillion by volume at 25 C. The manufacturer claims 100 parts per trillion by volume. The smallest sample actually analyzed in this calibration contained 1.6 picograms of benzene, corresponding to an atmospheric concentration of 0.3 parts per billion by volume.

The automatic column backflush feature was found to be of limited use without a temperature-controlled column enclosure. Valve times which cut off all peaks after toluene late one afternoon were too short to pass toluene the following morning because the column temperature was lower. Without controlled column temperature, backflush could be more of a nuisance than an advantage in field operation.

Multiple component calibration mixtures were prepared by static dilution of headspace vapors in ultra zero air were used to calibrate the unit for fourteen aromatic and halocarbon compounds. The retention time of bromobenzene, the least volatile of these, was less than thirty minutes at a carrier flow rate of 40 milliliters per minute.

Field sampling was carried out at several locations in the vicinity of Research Triangle Park, North Carolina. Apparent ambient background levels of benzene and toluene between the detection limit and 17 parts per billion by volume were observed. Trichloroethylene and 1,1,1-trichloroethane were also tentatively identified by retention times. The instrument could not be successfully operated unattended due to miscalibration problems.

A 0.53 millimeter (inside diameter) X 25 meter (length) fused-silica capillary column with a 5 micrometer chemically bonded methyl silicone stationary phase was installed. The backflush valves were bypassed, and the large diameter sample loop was replaced with a longer section of 0.81 millimeter (inside diameter) tubing having the same volume (1 milliliter). Flow lines were rerouted so the sample loop was normally in the carrier stream. Both short-term and long-term stability of detector responses was investigated and found to be more reproducible than were calibration standards made by static dilution of headspace vapors. Use of the capillary column resulted in a small improvement in resolution. However, tetrachloromethane was not resolved from benzene at a flow rate of 20 milliliters per minute. Dichloromethane and 1,1-dichloroethylene also were not resolved, and neither were 1,2-dichloroethane and 1,1,1-trichloroethane. Chromatographic resolution was not measured because of intermittent failure of the printer/plotter. The instrument had to be returned to the manufacturer for repair before further evaluation with the capillary column could be done.

The Operator's Manual provided limited information about how the instrument worked. For example, the instructions for setting integration parameters told nothing about how they influenced the integration process. Furthermore, when integrations were performed while operating at high gain, perpendiculars were dropped from the beginning and end of each peak to the level where the baseline had been at the beginning of the run. That was a reasonable procedure for early-eluting peaks which partially overlapped, but not for late-eluting peaks which were riding on an elevated baseline, and it lead to erroneous results. The Operator's Manual also contained several errors. For example, a linear relationship was alleged between duration of automatic injection and volume of sample injected. That relationship turned out to be more tenuous than linear. The Operator's Manual also suggested the instrument could reliably operate unattended, with retention times and response factors being corrected by periodic, automatic injections of calibrant. However, the wrong peak was often used for calibration, producing ludicrous results. Such mishaps were correctable by timely operator intervention, but this precluded unattended operation. Also, limits prescribed in the Operator's Manual for the length of time the solenoid valves could be activated were incorrect and obstructively misleading.

Laboratory evaluation of the Photovac 10S50 began at the end of February, 1986 and continued until the unit was returned to the manufacturer for repair of the printer-plotter in August, 1986.

RECOMMENDATIONS

It is recommended that the Photovac 10S50 be modified to provide the following improvements:

a. Controlled temperature (up to 40 C) in the column enclosure.
b. Standard use of fused-silica capillary columns.
c. A corrected and expanded Operator's Manual.
d. Revised software to provide:
    i. More reliable means of locating the calibrant peak.
    ii. Reporting of analyte concentrations lower than 0.001 parts per million.
    iii. An escape option when a wrong key has been pressed.
    iv. Increased operator control over peak integration methods.

It is also recommended that the modified instrument be subjected to further field testing to contrast results with those obtained simultaneously by Tenax/GC/MS and other methods.

SECTION 3

INSTRUMENT DESCRIPTION

The Photovac 10S50 is a microprocessor-driven portable gas chromatograph equipped with a photoionization detector and an automatic sampling system. It can be operated manually as a laboratory chronatograph, or, in automatic sampling mode, it can be continuously cycled to serve as a field monitoring unit. Data are output to a built-in printer-plotter. The unit is available (September, 1986) for $11750 from Photovac International Incorporated, 739B Park Avenue, Huntington, Long Island, NY 11743. The unit is intended primarily for industrial hygiene applications. A detection limit for benzene of 0.1 parts per billion by volume is claimed, and the instrument is said to detect some compounds which do not usually produce responses with a 10.6 electron-volt photoionization detector, including some saturated and unsaturated hydrocarbons.

PORTABILITY AND SIZE

"Portability" is a relative term. A pencil, for example, is portable. Entire analytical instruments usually are not portable, and moving them is difficult. Some instruments are semiportable. They can be mounted in a van or disassembled and moved from place to place. With care and luck, they may function properly afterward. Such instruments are not "portable". They are "transportable".

The Photovac 10S50 is a portable analytical instrument. It weighs approximately 12 kilograms (26 pounds) and is contained in an aluminum case 46 centimeters wide, 16 centimeters high, and 34 centimeters deep (18.25 inches wide, 6.25 inches high, and 13.25 inches deep). It can easily be carried with one hand. Preparations for moving the Photovac 10S50 include the following:

a. Disconnect external power (5 seconds).
b. Disconnect the carrier gas supply (5 seconds).
c. Charge the internal reservoir with carrier gas (2 minutes).
d. Install a can of calibrant gas in the holder and connect it, or use a separate calibrant cylinder and regulator (1 minute).
e. Close the lid, pick up the instrument, and go (10 seconds). Elapsed time is less than 5 minutes. At most, a 7/16 inch open end wrench is required, but finger-tight connections usually are sufficient.

Set up is similar:

a. Open the case and turn on the instrument (5 seconds).
b. Enter date and time in the microprocessor (30 seconds).

c. Check operating parameters and set gain (1 minute).
d. Connect the calibrant cylinder, if separate (1 minute).
e. Connect rotameters to carrier outlets and check flows (5 minutes).
f. Start operation five minutes after the "READY" indication.

Elapsed time is less than 10 minutes. The Photovac 10S50 is slightly less "portable" than a portable typewriter.

UTILITIES AND SUPPLIES

Electric power from an external 110 or 230 volt, 50 or 60 Hertz alternating current power source is required for charging internal and external 12 volt batteries. The internal battery can provide power for at least four hours of operation. An external battery extends operational capability beyond the length of a work day with all power consuming options in use. The power cables furnished with the external batteries also can be plugged into an automobile cigaret lighter. External batteries are alleged to be at risk of damage if left charging indefinitely, but no actual harm seems to result from doing so. The internal battery is under microprocessor control and cannot be overcharged. When it discharges to a lower limit, the microprocessor turns off the unit automatically to protect the batteries and to conserve power for maintaining nonvolatile memory. Once automatic shut-down has occurred, external line power is required to restore operation. Use of an external battery with a discharged internal battery is not possible. The internal battery does not discharge significantly during day long operation on external battery power, but discharge becomes significant once the voltage of the external battery falls below that of the internal battery. It is good practice to leave external line power connected when the unit is not in use so the internal battery will be fully charged when needed. It recharges any time the unit is connected to external line power.

Carrier gas, normally ultra zero air, can be supplied from an external cylinder through a 0.125 inch quick-connect fitting. Supply pressure must be regulated to 40 pounds per square inch. For field operation, a one day supply of carrier gas can be injected into the internal tank through a 1/4 inch quick-connect fitting with a special valve and hose assembly available from Photovac. Pressure from the internal tank is controlled by an internal regulator which has been factory set to 40 pounds per square inch. Ultra zero air (less than 0.1 part per billion organic material, measured as methane) is required because of detector sensitivity. Zero air is not pure enough and causes the detector to operate near saturation, resulting in dramatic and apparently mysterious loss of dynamic range. Other more usual carrier gases such as helium or nitrogen also can be used. The advantage of using air is that the sample matrix remains unchanged. Carrier flow rates are measured with an external rotameter and controlled by two needle valves mounted on the instrument panel.

The printer consumes ordinary 2.25 inch (width) adding machine tape. It uses Tandy plotter pens in red, blue, green, and black which can be purchased from Radio Shack stores.

INSTRUMENT CONTROLS

All operations are performed through a 16 kilobyte microprocessor which monitors the charge of the internal battery and controls the detector, the cycling of flow control valves, the processing and printing of data, and the application of peak recognition parameters. Operator input to the microprocessor is made through a mnemonically-labelled keypad on the control panel (Figure 1). Nonvolatile memory includes four Analytical Libraries, each with a capacity of twenty-five entries. Compound names, relative retention times, and response factors are stored by the operator as library entries and updated by the microprocessor following calibration runs. Operating parameters also are stored in each library. When the unit is turned on, printer instructions, peak recognition parameters, minimum peak area, peak window, valve sequencing, and run cycling are under control of the current library. At power-up the current library is the one which was in use when the unit was turned off. Gain at power-up is set to its minimum level of 2 and must be reset to the required level. Date and time start from the moment the unit was turned off and must be reset after power-up. All other operating parameters are set by the current library. Each library carries its own separate set of operating parameters, and this should be kept in mind when changing from one library to another. A liquid crystal display (LCD) on the control panel shows messages and prompts and echoes key-press entries.

FLOW SYSTEM

Carrier flow path and automatic sample injection are controlled by six solenoid valves. Air is sampled by pumping it through a 17 centimeter length of 2.74 millimeter (inside diameter) Teflon tubing (total volume 1 milliliter) immediately prior to injection. Injection occurs when solenoid valves on each end of the sample loop are activated to admit carrier flow. Samples can also be injected through a septum with syringes. A 0.125 inch X 4.5 foot packed column and a 6 inch precolumn are original equipment. The precolumn has the same diameter and contains the same packing as the main column. It can be backflushed, starting at a preselected time after injection, to prevent compounds less volatile than those being analyzed from entering the main column and delaying or interfering with subsequent runs. By the time the last compound sought has eluted from the main column, all less volatile material has long since been backflushed out of the precolumn.

A detailed plan of the flow system is shown in the Operator's Manual (Figure 2). Careful scrutiny revealed no discrepancies between Figure 2 and the actual unit. There are numerous ways of rerouting flows for different kinds of operation. Several ports and many of the flow lines are installed but left unconnected when the instrument is manufactured. They are provided to facilitate modifications. Valve No. 6 (at the bottom right of Figure 2) controls injection of pressurized calibrant. Valves No. 1 and 4 switch the

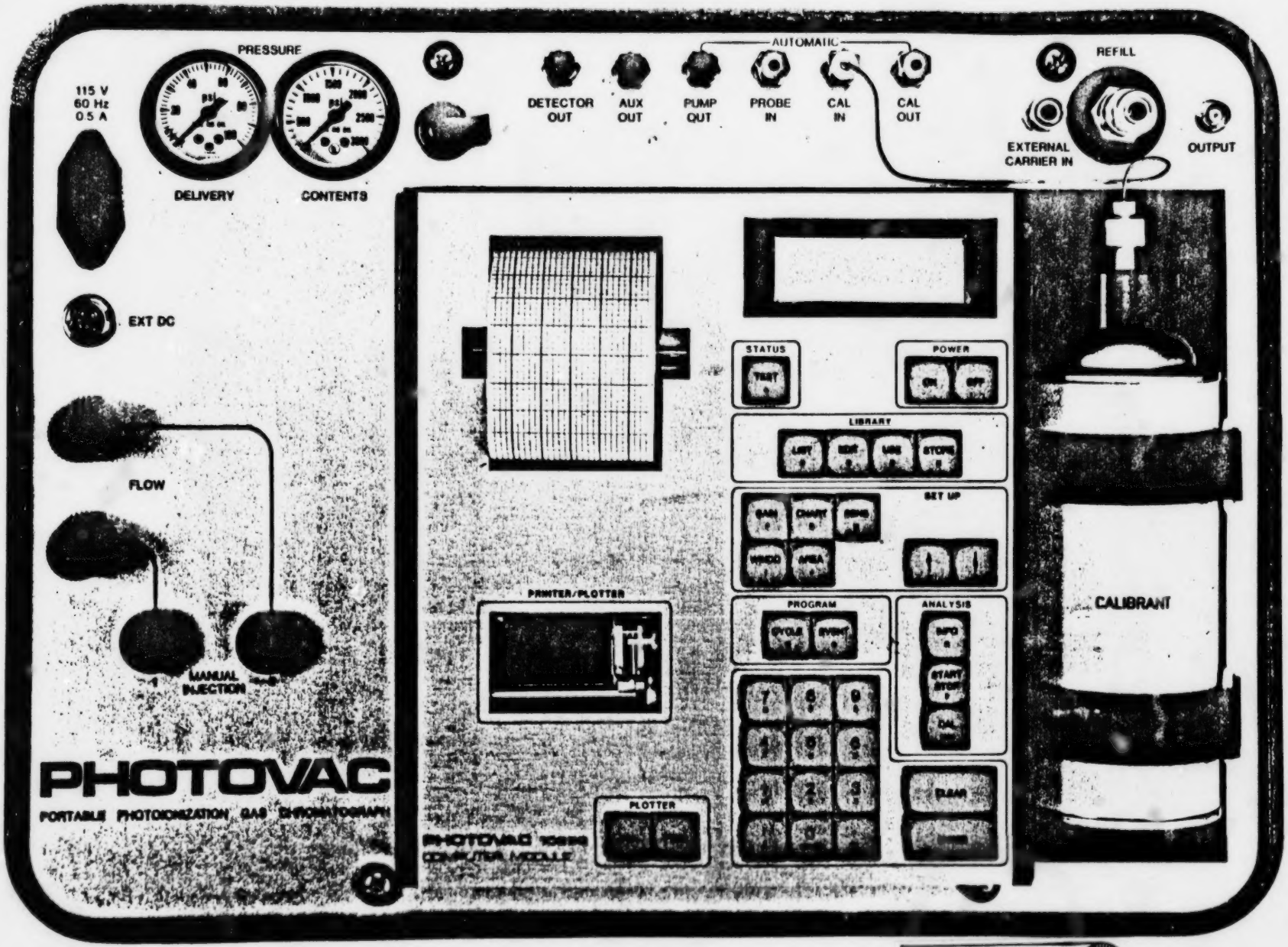

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Figure 1. Top panel of Photovac 10S50.

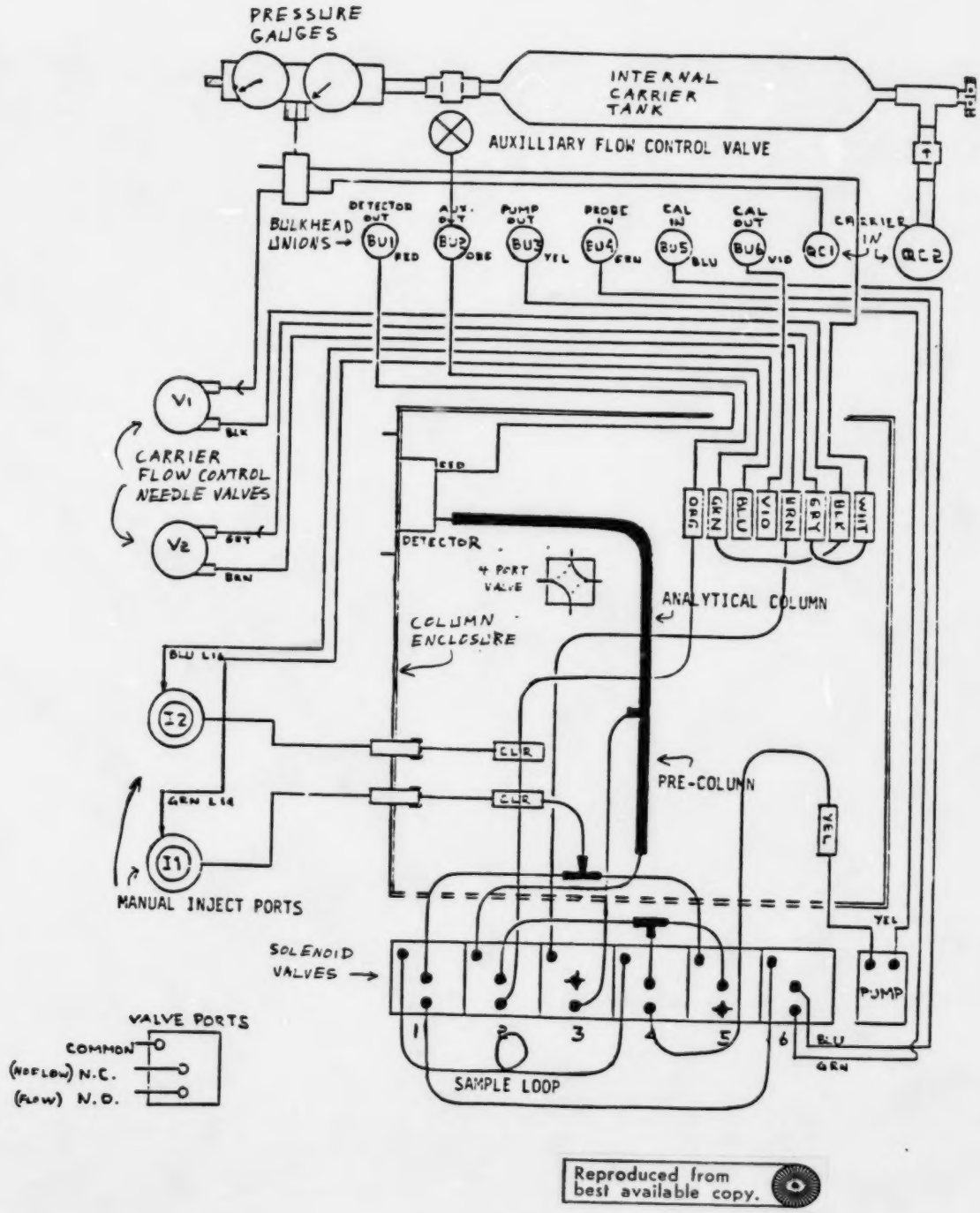

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Figure 2. Flow diagram of Photovac 10S50 set up for precolumn backflush operation.

injection loop in and out of the carrier stream. Valves No. 2 and 3 control direction of flow through the precolumn. Valve No. 5 is used to send carrier gas past the sample loop when backflush is off.

Valve sequencing is controlled through "Events" stored in the library. Event "ON" and "OFF" times are set by pressing the "EVENT" key and entering the Event number. Prompts for the "ON" and "OFF" times appear on the LCD. Event No. 1 is operation of the sample pump. It operates if "sample" mode has been selected. If "calibrate" mode has been selected, Event No. 2 operates, opening Valve No. 6 to release calibrant into the sample loop for a preset interval. Event No. 3 turns "on" Valves No. 2 and 3 which send carrier gas through the precolumn in the "forward" direction. Event No. 4 activates Valves No. 1 and 4 at either end of the sample loop to place it in line with carrier flow. Event No. 5 activates Valve No. 5 to send carrier gas around the sample loop when it is out of the carrier stream and backflush is not operating. Valves No. 1 and 4 always operate together, as do Valves No. 2 and 3.

A typical "sample" run begins with a 10 second interval during which ambient air is drawn through the sample loop by the pump. Then Event 1 ends (the pump stops), Event 3 begins (forward flow of carrier through the precolumn), Event 4 begins (flow of carrier through the sample loop), and plotting of the chromatogram begins. After 1 second, Event No. 4 ends (sample loop is removed from carrier flow), and Event No. 5 begins (carrier gas bypasses the sample loop). After desired compounds have cleared the precolumn, Events No. 3 and 5 end (precolumn backflush is restored). A typical "calibration" run differs from a "sample" run only in that Event No. 2 (injection of calibrant through the sample loop for one second, ending one second before injection) is substituted for Event No. 1. Syringe injections are done by setting Event No. 4 "ON" and "OFF" times to zero and Event No. 5 "ON" time to 10 seconds (the same as Event No. 3 "ON" time). Injection is made immediately after the pump stops.

COLUMN ENCLOSURE

The chromatographic column is contained in an insulated enclosure which can be opened by turning a knob at the back of the top panel and lifting the left side of the control module. A 0.125 inch X 4.5 foot Teflon column packed with 5% SE-30 on 100/120 mesh Chromosorb G was supplied with the unit. The enclosure is rectangular, measuring 18.5 X 19 X 3 centimeters (7.25 X 7.5 X 1.125 inches). Its layout is shown approximately in Figure 2. The handle of a four-way valve protrudes into it from the bottom near its center. Four bulkhead fittings are mounted in the left hand wall. Two of them introduce lines from the injection ports and the other two are the inlet and the outlet to the detector. A 7.5 X 0.5 centimeter (3 X 0.25 inches) opening at the top of the front side provides access to the solenoid valves, which are mounted in a row immediately outside. Though it is insulated, the enclosure is not temperature-controlled, and it is subject to casual heat flow, especially from the solenoid valves and the detector.

DETECTOR

The detector has a volume of 200 microliters and uses 10.6 electron-volt ultraviolet light from an electrodeless radio frequency coupled discharge lamp. The gas mixture in the lamp is proprietary. Light of 10.6 electron-volts energy is capable of ionizing many organic compounds. Compounds which have ionization potentials greater than 10.6 electron-volts, such as unsaturated and saturated hydrocarbons, are often ionized as well. This results from double photon absorption events which are relatively common in this detector because of the extremely high photon flux of the lamp. Nevertheless, water and noble gases are not ionized, so interferences from them do not occur. Ionization of air components generally causes no interferences because the sample matrix is substantially the same as the carrier gas. Positive ions are collected on an electrode maintained at a potential of -300 volts, and the resulting ion current is amplified. Power supply to the detector, electrode potential, and measurement of ion current are controlled by the microprocessor. The detector temperature is not thermostatically controlled, and it undergoes a brief warm-up period before output stabilizes.

CALIBRATION

Calibration is normally accomplished by sampling a calibration gas mixture which has been passed from a cylinder through the sample loop under elevated pressure and then equilibrated to atmospheric pressure. Authentic samples in dry nitrogen with certified concentrations in the part per trillion to part per million range are available from vendors. For some compounds these mixtures can be certified traceable to an NBS SRM. Linear response is assumed, and single point calibrations are used. Verification of linear response is described in Section 4, Evaluation.

DATA PROCESSING

All data are output to the printer-plotter. A connector for an optional strip chart recorder is provided. It carries a signal which has been digitized by the microprocessor and then reconverted to analog. Thus the strip chart recorder merely provides a copy of the same output supplied to the printer-plotter. The printer-plotter provides a chromatogram trace and a quantitation list on paper tape 2.25 inches wide.

A real time trace of the chromatogram is drawn by the printer-plotter (Figure 3). At the beginning of a run the starting point is marked. Positive perturbations of the baseline which meet peak recognition criteria are assigned peak numbers. Peak areas which exceed an operator preassigned minimum are reported. The microprocessor estimates the areas of off-scale peaks by triangulation. The baselines used in integration can be plotted,

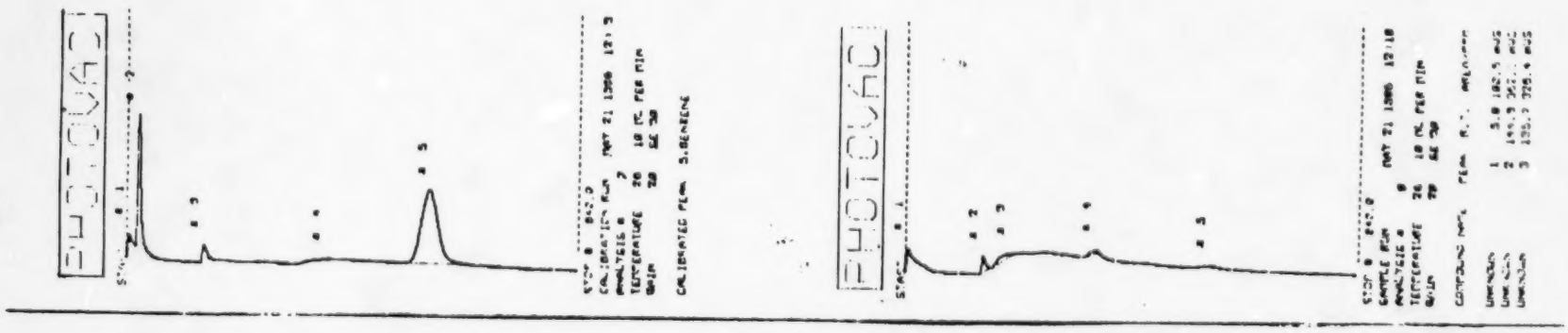

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Figure 3. Output plot from Photovac 10S50 showing a calibration run and a sample of room air.

if requested. When the retention time of a peak falls within the window of a library entry, the peak is "identified" and quantitated. If it falls within more than one window, the library entry having the closest retention time is used. After the end of the chromatogram has been marked, run parameters and peaks are listed. Areas of "identified" peaks are given in units of parts per million by volume. If the compound exceeds an operator preset concentration it is flagged by printing "PPM" in red. Areas of unidentified peaks are given in units of millivolt-seconds or volt-seconds.

AUTOMATIC CYCLING

Automatic cycling of the unit including sampling, analysis, and computing time weighted averages of the data, is started and controlled through the keyboard. Pressing the "CYCLE" key initiates a series of prompts which appear on the LCD. These request instructions for "PLOTTER DELAY" (seconds after the start of a run before injection), "ANALYSIS TIME" (duration of the chromatogram in seconds), "CYCLE TIME" (minutes between injections), "CAL ON CYCLE" (number of sample runs between calibration runs), calibrant information (its serial number in the library list and its concentration in the calibrant mixture), and "TWA ON CYCLE #" (the number of runs to do before printing time weighted averages of all compounds in the library). Once a nonzero "CYCLE TIME" has been entered and all prompts answered, the time-weighted averages are reset to zero and the unit is ready for automatic cycling. Cycling begins when a run is started and continues until stopped by low batteries, by operator intervention, or by completion of a preset number of cycles (entered by pressing the "OFF" key).

SECTION 4

EVALUATION

The Photovac 10S50 was evaluated as a monitor for organic compounds in ambient air. Evaluation consisted of testing the capabilities of the unit, initially by connecting it to utilities and turning it on, and then by examining its performance features as described in the Operator's Manual. These features included peak resolution and integration, calibration, benzene detection limit, reproducibility of analyses, and operation with a capillary column. Performance under field operating conditions also was observed.

BACKFLUSH OPERATION

As supplied, the instrument was set up for precolumn backflush operation. Except during the period immediately following an injection, carrier flow was split, half of it passing backward through a short precolumn and the other half passing forward through the main column. At the time an injection was made, this flow pattern was changed by operation of solenoid valves so that the carrier flow passed through the precolumn in the forward direction and then forward through the main column. After a preset interval, backflush was resumed. This resulted in relatively volatile compounds passing through the main column, while heavier ones were eliminated by backflushing them from the precolumn. This prevented their delaying or disrupting subsequent analyses and was potentially a significant convenience when sampling grossly contaminated air.

In preparing to operate the unit it was necessary to determine how long to wait after injection before resuming backflush. The Operator's Manual recommended that valve activation times be limited to 50 seconds or less, but analysis of heavy compounds such as chlorobenzene required much longer times, even at a carrier flow of 40 milliliters per minute. The 50 second limitation turned out to be incorrect, having been applicable to valves used in an earlier version of the unit. It was found that valve settings which cut off all peaks after toluene late in the afternoon were usually too short to pass toluene the following morning because the column temperature was lower. Without temperature control of the column enclosure, backflush could be more of a nuisance than an advantage in field operation. Even slight changes in ambient temperature caused problems.

PEAK INTEGRATION

Peak integration was controlled by three parameters set by the operator and stored in the microcomputer library. The LCD prompted for them when the

"SENS" key was pressed. They were "SLOPE UP" (the minimum rate of increase in output signal which would cause the microprocessor to recognize the beginning of a peak), "SLOPE DWN" (the rate of decrease in output signal which would cause the microprocessor to recognize the end of a peak), and "PW @ 4 MIN" ("the width of a peak eluting four minutes after injection"). No description was given in the Operator's Manual of the effect these parameters had on peak integration. Setting of "SLOPE UP" and "SLOPE DWN" seemed obvious, yet they did not result in integrations beginning and ending at those points on the trace. The way in which they were used was modified by the "PW" parameter. Its purpose was to control a gradual decrease in the rate at which data were taken, so that the number of points stored for broad, late-eluting peaks would not exceed the capacity of the microprocessor. An unexpected effect of setting this parameter to the actual widths of peaks eluting at about four minutes (an obvious temptation) was that it seemed to keep the microprocessor from recognizing the end of one peak until the next one appeared. That kept integration of the last peak from being completed unless a noise spike happened to follow it. When questioned about this, the manufacturer suggested that "SLOPE UP", "SLOPE DWN", and "PW" be set to 10, 10, and 2, respectively, and those settings usually worked well. It would have been helpful if the Operator's Manual had given more guidance for setting these parameters and more information about the way they affected integrations.

When integrations were performed while operating at high gain, perpendiculars were dropped from the beginning and end of each peak to the level where the baseline had been at the beginning of the run. That was a reasonable procedure where early-eluting peaks were partially overlapped, but not for late-eluting peaks which were riding on an elevated baseline. In that case, true peak area was often a small fraction of reported peak area, resulting in large concentration errors. This problem is potentially very serious in operating the instrument unattended or while obtaining time-averaged results without plotting chromatograms.

PRESSURIZED CALIBRATION STANDARDS

The Photovac 10S50 is intended normally to be calibrated by passing a standard calibrant mixture from a pressurized container through the sample loop. Standards consisting of part per billion to part per million mixtures of analytes in dry nitrogen are available from vendors. This method of calibration is convenient to use and consistent with the design of the instrument, but obtaining such standards may require substantial time and involve considerable expense. Storage stability of any calibration mixture can be extremely limited unless a proper container has been used. Pressurized standards used in this study were Standard Reference Materials from the National Bureau of Standards (NBS SRM No. 1805 and No. 1811). This method of calibration is directly compatible with the way data are reported by the microprocessor, and the calibrant is treated in the same way as any other sample, which eliminates many potential sources of systematic error. Recalibration during field operation must be done in this manner.

PREPARATION OF CALIBRATION STANDARDS BY STATIC DILUTION

When pressurized standard mixtures were unavailable, library entries were created by use of calibration standards prepared by static dilution of headspace vapors. A flask of known volume was flushed with ultra zero air and capped with a Mininert Valve. Room temperature was noted, and headspace vapors were injected into the flask with gas tight syringes. Concentrations were calculated from vapor pressure data by plotting the logarithm of pressure versus the reciprocal of absolute temperature (2). The slope and intercept of the resulting linear plot were calculated by the method of least squares. These parameters were used to calculate the concentration of headspace vapor at room temperature. Fresh calibration mixtures, prepared daily, deteriorated slowly enough to be usable all day. The syringes used to measure headspace vapor were cleaned by heating them to about 100 C for at least 15 minutes. Detector responses (volt*second) were matched with masses of compounds (picograms) in the resulting calibration tables. This kind of calibration was useful for work in which syringes were used in sampling. Standard mixtures prepared by static dilution apparently were reproducible to within about 50% of nominal concentrations, and that should be considered when interpreting results. Use of certified pressurized standards is clearly preferable.

In order to use static dilution mixtures to calibrate for automatic sampling, the masses of material (picograms) injected by syringe into the chromatograph were converted to the equivalent concentrations (parts per million by volume), using the ideal gas law. The injection volume was calculated as recommended in the Operator's Manual, but it was found that responses to injections through the sample loop were always much greater than responses to syringe injections calculated to be the same size. This discrepancy resulted because the method given in the Operator's Manual for calculating volume injected from the sample loop was in error. That method was to multiply the time the sample loop was in line with the carrier flow by the rate of carrier flow divided by 60. Assuming constant flow, it would have been reasonable and dimensionally correct:

(loop time)*(flow rate)/60

(seconds)*(milliliters/minute)/(seconds/minute) = milliliters

This calculation did not take account of the large pressure surge which occurred when the valves were operated. It perturbed the baseline and was seen at the downstream end of the column as a two- to four-fold transient increase in flow rate. It caused injection of a much larger portion of the volume in the sample loop than was predicted by the calculation.

A more accurate method of determining loop injection volume was to compare the response of the instrument to loop injection with its response to syringe injections of the same standard. A flask was flushed thoroughly

with NBS SRM No. 1805 (0.254 parts per million benzene in nitrogen) and then capped with a Mininert Valve. Aliquots of different sizes were injected and a plot of volume injected (microliters) vs. detector response (volt*second) was made. This plot was linear over the entire range of volume with a correlation coefficient of 0.998 (Figure 4). Loop injection volume was then determined by sampling the SRM through the calibration port and comparing the response with the plot. Results are summarized in Table I.

TABLE 1. ACTUAL AND CALCULATED INJECTION VOLUMES (a)

Flow Rate ml/min	Slope ul/volt*sec	Intercept ul	Volume Actually Injected ml	Calculated Injection Volume ml
10.0	2.96	40.7	1.50	0.17
20.0	3.14	46.6	1.16	0.33
30.0	3.34	53.7	1.10	0.50
40.0	3.67	42.8	0.87	0.67

a. Sample loop in line with carrier stream for 1 second.

The discrepancy between calculated and true volumes was almost an order of magnitude at 10 ml/min and decreased with increasing flow rate to about 30% when the carrier flow rate was increased to 40 milliliters per minute. Injection of a volume larger than the measured size of the sample loop may have been due to volume in the solenoid valves which was not reckoned in calculating injection volume from the dimensions of the tubing from which the loop was constructed. Larger injection volumes than 1.5 milliliters did not result when loop time was increased above 1 second. Such a discrepancy between calculated and actual injection volumes could be a source of error if the unit were calibrated by syringe injection from a static dilution bottle. However, if calibration were done using pressurized standards, as recommended in the Operator's Manual, the problem could not arise. Figure 4 shows linearity of response to benzene over a range from 125 to 750 parts per billion by volume.

ANALYTICAL LIBRARIES

Nonvolatile memory in the microprocessor included four Libraries, each of which controlled the operating parameters (except gain) and had a capacity of twenty-five compounds. The library entry for each compound included its name, retention time, response factor, and warning level (the level above which it would be flagged on the print-out). Library entries were created by running a chromatogram and then entering information on individual peaks (identified by peak number) following prompts from the LCD. Library entries could be updated after each calibration by specifying the peak number of the calibrant, its library number, and its concentration. If

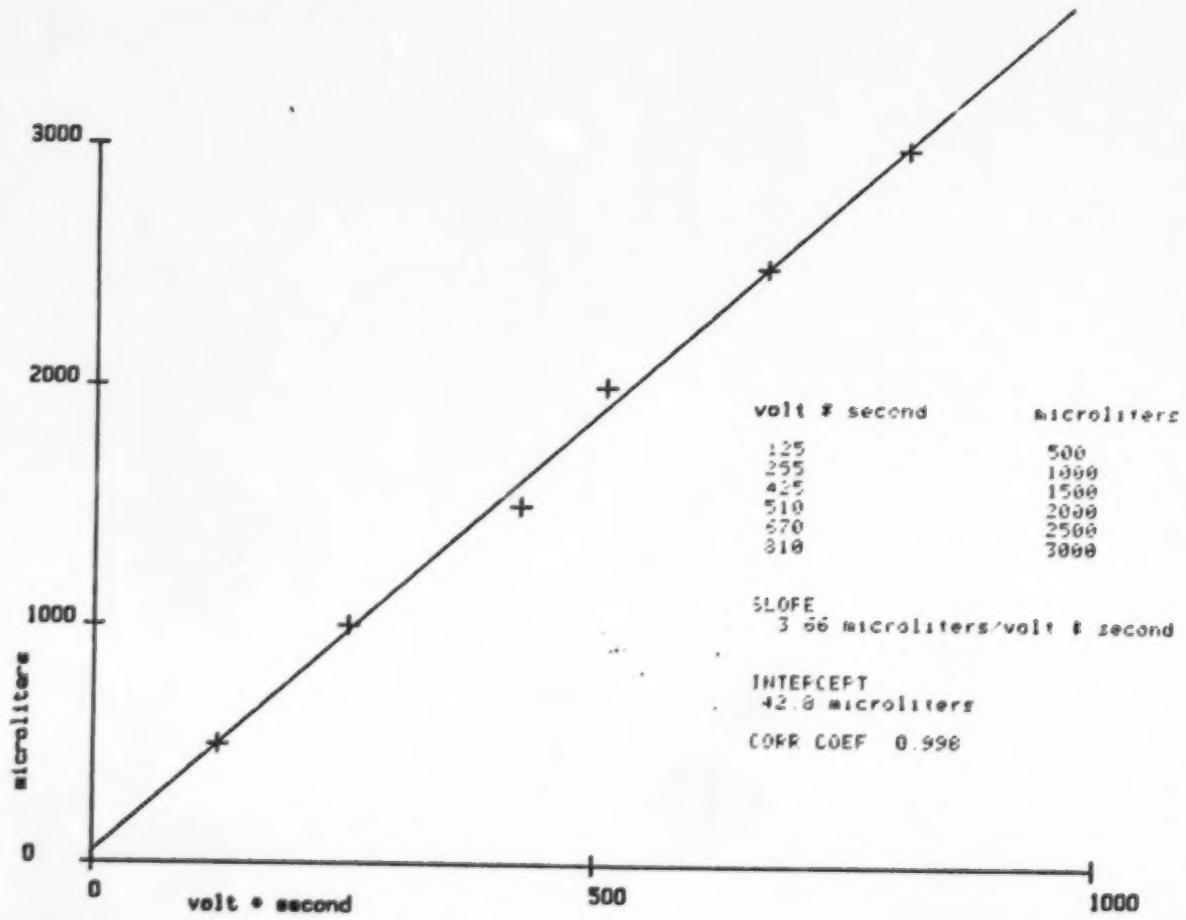

Figure 4. Volume of NBS SRM No. 1805 injected with a gas-tight syringe (microliters) versus response (volt * second).

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a concentration of zero was specified, only the retention time was updated. Recalibration of one compound resulted in proportional corrections to all library entries. This made it possible to use one compound in each library as an internal calibration standard for the entire library. During continuous cycling, all corrections were made automatically after each calibration run.

In the first calibration, fourteen compounds were divided into four groups, each of which eluted quickly at the flow rate used. These groups are listed in Table II with their respective carrier flow rates, concentrations, and retention times. These concentrations were selected to produce large peaks which were not off scale at a gain of 20. Thus the concentrations reflect the differences in sensitivity to the detector among these compounds. The compounds marked with asterisks served as group calibration standards.

BENZENE DETECTION LIMIT

A data acquisition program was used to monitor analog output from the unit with a Hewlett-Packard Model 85 computer through a Hewlett-Packard Model 6942A multiprogrammer interface equipped with an analog-to-digital converter. Detector output signal was sampled at intervals of 0.2 second and stored in memory for further processing. At the end of the run a portion of the chromatogram which included the calibrant peak was displayed on the screen. Start and end points of the peak were determined by inspection and input manually. The program then drew a straight line between them, and determined peak area by summing the heights above the line of all data points from the beginning to the end of the peak. In addition, the standard deviation of the 40 baseline points immediately before the beginning of the peak plus the 40 baseline points immediately after the end of the peak was calculated. Aliquots of NBS SRM No. 1805 (0.254 parts per million of benzene in nitrogen) were injected with gas tight syringes at a constant gain of 50, and data for each injection were stored on disk. Another program was used to retrieve the data, and a plot of peak area (volt*second) versus amount injected (picograms) was generated. The data were subjected to linear regression analysis. The programs used are listed in Appendix A, and the data are listed in Table III and plotted in Figure 5.

The slope of the plot was 0.502 volt*second/picogram with an intercept of 6.4 volt*second and a correlation coefficient of 0.999. This plot shows linear response over a range from the detection limit to 125 parts per billion by volume. The aggregate standard deviations of the baselines of all peaks was 0.0238. The detection limit was taken to be twice the aggregate standard deviation of the baselines divided by the slope, or 95 femtograms. It was equivalent to a concentration of 0.03 parts per billion by volume of benzene at 25 C, which was lower than the manufacturer's claim of 0.1 part per billion and much lower than required to detect 1 part per billion of benzene in air. This was an extrapolated detection limit, the smallest sample actually injected being 1.63 picograms. Probably a lower detection limit could have been attained if smaller samples could have been taken, but the practical lower limit of sample size was defined by a persistent artifact on the baseline at the retention time of benzene.

TABLE 2. CALIBRATION WITH PACKED COLUMN (a)

Library Number	Compound	Flow (milliliters per minute)	Concentration (parts per million) (b)	Retention time (seconds)
1	1,1-Dichloroethylene	10	0.33	153.3
	Dichloromethane		2.20	161.9
	Trichloromethane		24.5	338.0
	1,2-Dichloroethane		10.3	425.9
	1,1,1-Trichloroethane		4.65	450.1
	benzene (c)		0.239	517.3
2	Trichloromethane	20	27.3	198.9
	1,2-Dichloroethane		11.4	247.8
	1,1,1-Trichloroethane		5.17	263.2
	Benzene		0.266	299.8
	Tetrachloromethane		15.3	313.1
	Trichloroethylene		0.206	422.9
	Toluene (c)		0.227	783.7
3	Benzene	30	0.295	242.5
	Tetrachloromethane		15.4	247.7
	Trichloroethylene		0.228	340.4
	Toluene		0.253	631.7
	1,2-Dibromoethane		0.846	781.8
	Tetrachloroethylene		0.172	940.8
	Chlorobenzene (c)		0.704	1232.8
4	Toluene	40	0.288	389.5
	1,2-Dibromoethane		0.964	479.8
	Tetrachloroethylene		0.196	573.5
	Chlorobenzene		0.797	751.1
	o-Xylene		1.153	1184.1
	Bromobenzene (c)		0.743	1534.1

a. 0.125 inch X 4.5 foot packed with 5% SE-30 on 100/120 mesh Chromosorb G. Six inch precolumn.

b. Concentrations were chosen to produce large, on-scale peaks at a gain of 20.

c. Compound used as group reference standard.

TABLE 3. BENZENE DETECTION LIMIT (a)

Mass of Benzene (picograms)	Response (volt*second)
408.	210.
327.	167.
245.	137.
163.	86.9
81.7	44.5
40.8	26.0
20.4	17.1
8.17	14.2
4.08	10.6
1.63	2.27

Summary of Linear Regression Analysis:

Slope = 0.5016 volt*second/picogram
Intercept = 6.385 volt*second
Correlation Coefficient = 0.999
Aggregate Standard Deviation of the Baseline = 0.0238
Extrapolated Detection Limit = 0.0947 picogram

a. 0.125 inch X 4.5 foot packed with 5% SE-30 on 100/120 mesh Chromosorb G. Six inch precolumn.

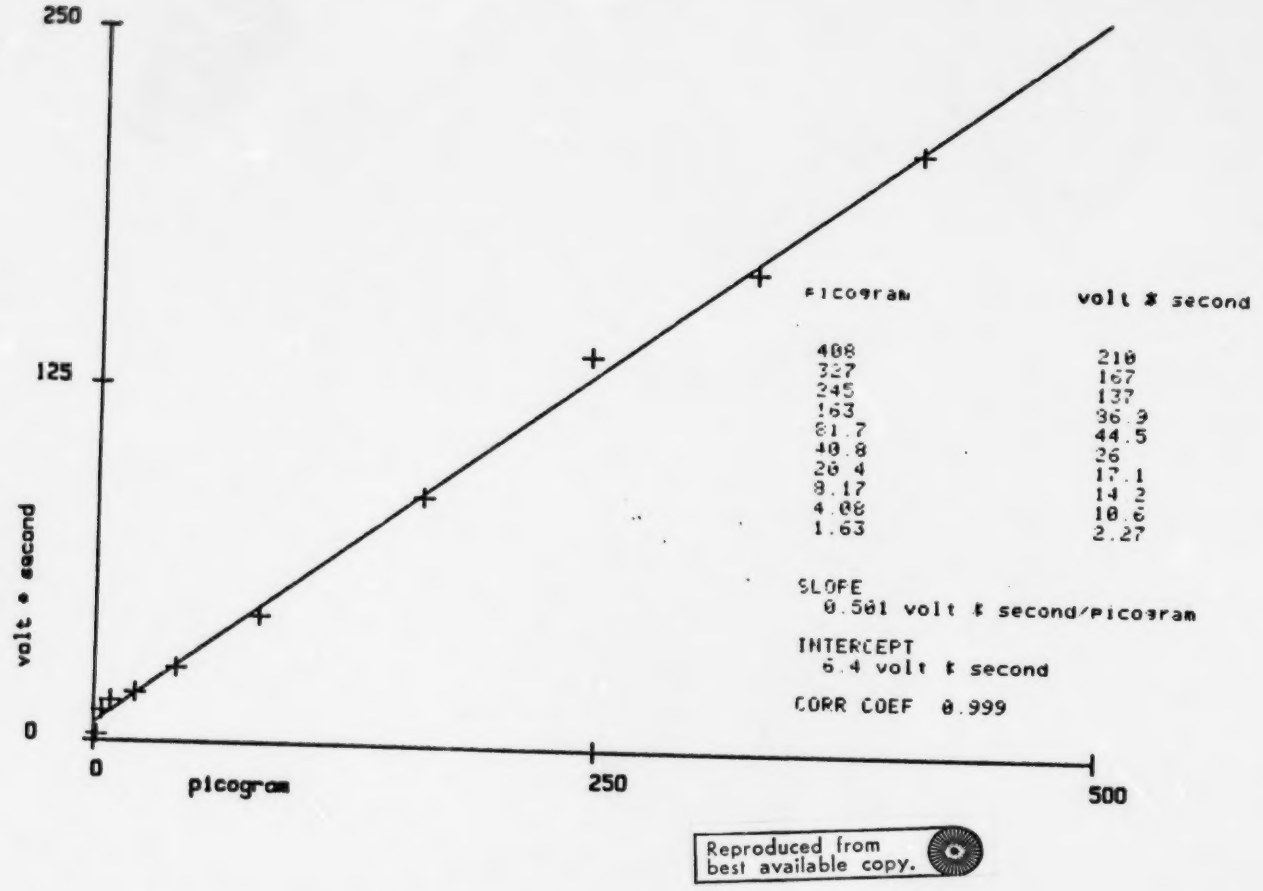

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Figure 5. Response to aliquots of NBS SRM No. 1805 (volt * second) versus mass of benzene injected (picograms).

Likely this actually was benzene, present as a low level contaminant originating from the automatic calibration procedure. The extrapolated detection limit of 95 femtograms was lower than the value of 800 femtograms obtained by Clark and coworkers who used a Photovac 10A10 chromatograph with the same detector (3). Their detection limit was determined differently ("2.5 times the signal-to-noise ratio"), which may account for some of the difference in the values. It was higher than the extrapolated detection limit of 17 femtograms obtained in this laboratory with a Photovac 10A10 instrument using the same method. The lower practical limit of 1.63 picograms due to the artifact was equivalent to 0.5 parts per billion, and it represents the worst-case performance. Perhaps use of a different calibrant would eliminate this problem. Detection limits for other compounds would vary inversely with their relative sensitivities to the photoionization detector. Relative sensitivities were not determined, but the concentrations used in the calibrations (listed in Table II) provide good indications of them because they were chosen to give peaks of about the same size at the same gain. It should be remembered that no estimate of detection limit can anticipate complications which may arise during operation in the real world. Nevertheless, it is apparent that this unit, as-is, should easily be capable of detecting the part per million or lower levels of benzene, benzene derivatives, and halocarbons which raise concern about public health when they are found near hazardous waste sites and other sources.

REPRODUCIBILITY

Extraneous peaks were found in all of the calibration gases. The number of them was variable and unpredictable. Because the calibrant peak was identified solely by elution order, they caused misidentification and limited the feasibility of unattended operation. The calibration gas regulator was of high purity type, so it was not the cause of the problem. Transfer lines made of fluorinated ethylene and propylene (FEP) Teflon or stainless steel were used, and two different NBS Standard Reference Materials (Nos. 1805 and 1811) were tried without eliminating the problem. There was little more that an ordinary laboratory could do to ensure reliable calibration. When output was monitored with the Hewlett-Packard Model 85 computer it could be seen that some of the "extra" peaks which fouled the calibration actually were noise spikes. Each of these was interpreted as a peak by the microprocessor and assigned a peak number. There were very few noise spikes, but only one was needed to cause a peak miscount and produce a miscalibration. When either internal or external batteries were relied upon exclusively for power during analyses the occurrence of noise spikes was reduced. Most of the data in this report were obtained while operating on battery power, and no battery-related failures occurred. However, this did nothing to eliminate random appearance of extra peaks from the calibrant gas. When they occurred, some peak other than benzene received the peak number assigned to benzene. The retention time of the peak was not considered by the microprocessor in making this assignment. Once this had occurred, the peak was recognized as "benzene". Its area was matched with the concentration information for benzene being used by the microprocessor. Typically, the peak would be much smaller than benzene and necessarily would have a different retention time. This put the

unit catastrophically out of calibration until the next time it happened to find the benzene peak during a calibration run. The only means of preventing such errors was timely recognition of the problem by the operator, followed by appropriate corrective action. Miscalibration could cause serious errors in time weighted averages of results obtained during unattended operation.

FIELD OPERATION WITH PACKED COLUMN

After calibration, the unit was used to sample laboratory air. Concentrations of benzene between 0.001 and 0.003 parts per million by volume were found, but no other compounds. Grab samples were collected at various locations in Durham and Orange Counties, North Carolina, by flushing out a Pyrex flask with local air, sealing it with a Mininert Valve, and returning it to the laboratory. Aliquots were injected into the unit. Very small peaks were occasionally seen, but no positive results were obtained by this method. The small quantities of compounds present in these samples may have been reduced below minimum peak area at a gain of 20 by adsorption onto the walls of the flask.

The unit also was operated at nine locations near Research Triangle Park, North Carolina. The results obtained at eight sites are summarized in Table IV. Background levels could not be seen because gain could not be set higher than 20 without sending the calibrant peak off scale. Use of lower calibrant concentration would have enabled detection of ambient vapors at lower levels, but the unit, as presently configured, cannot report concentrations below 0.001 parts per million. The microprocessor could have been "fooled" by assigning a calibrant concentration N times higher than the true value and then manually dividing all data by N, but that was not done in this study. Four compounds apparently were detected in the field study. These were benzene, toluene, 1,1,1-trichloroethane, and trichloroethylene. It must be emphasized that these identifications are TENTATIVE, since they are based only on retention times. Compounds of similar volatility and polarity could have been present. Nevertheless, the compounds tentatively identified could not actually have been present in concentrations larger than indicated.

The ninth sampling location was the roof of the CAMIO Station on South Roxboro Street in Durham. The sampler was run there all day on Friday, June 6, 1986, but no results were obtained because the unit was left strictly unattended. The sampler was shaded, but the calibration gas cylinder was not. As the sun heated it, the number of extra peaks increased dramatically, so that the correct peak was used only on the first calibration.

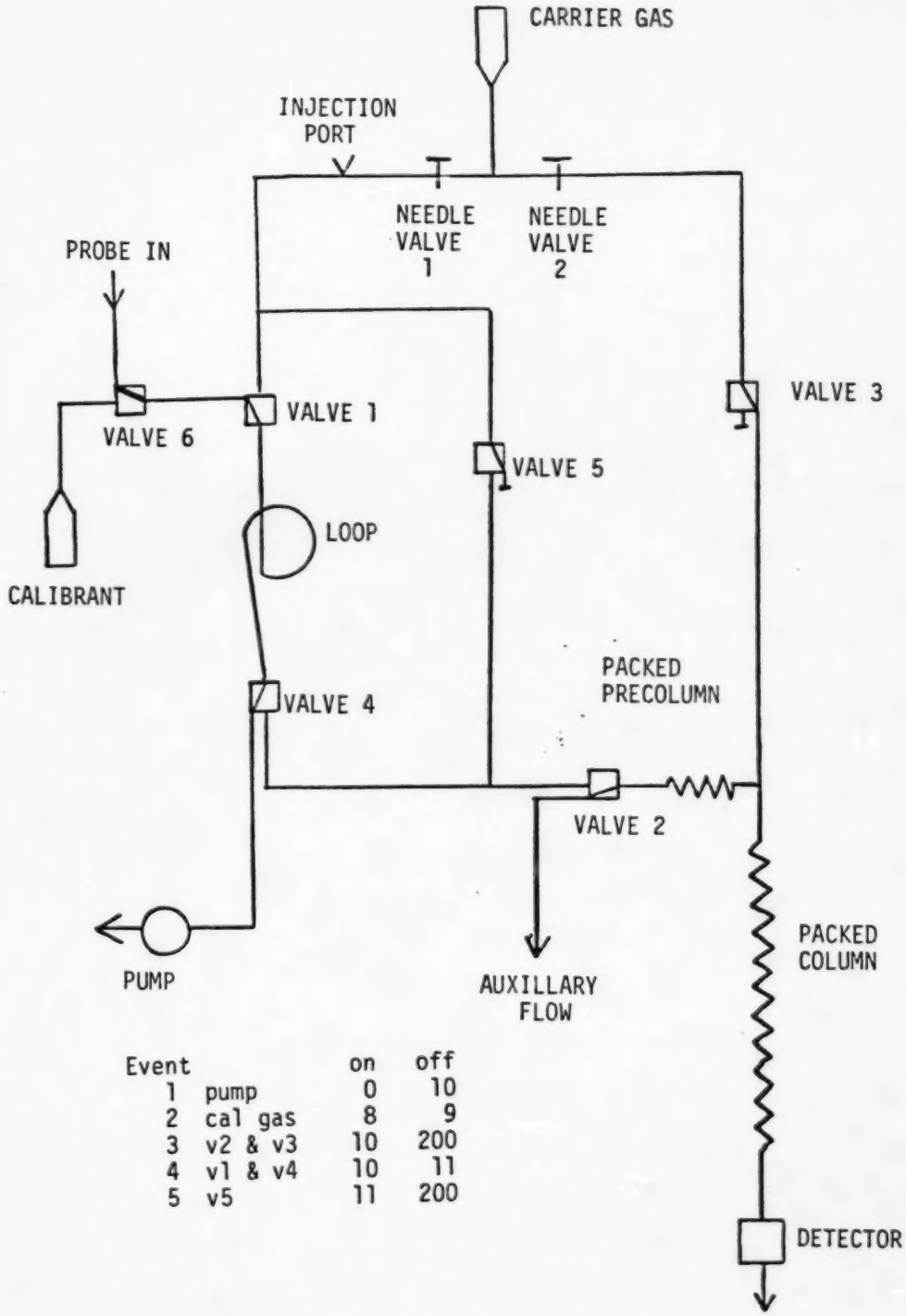
CAPILLARY COLUMN OPERATION

A 0.53 millimeter X 25 meter fused silica column with a 5 micrometer chemically bonded methyl silicone phase was installed after completion of field evaluation. This column had to be rewound on a 6.5 inch diameter spool which was hand made from styrofoam sheet and pasteboard to fit the column enclosure. The backflush valves were bypassed. The precolumn

TABLE 4. FIELD SAMPLING RESULTS

Date/Day Compounds	Concentrations found in consecutive analyses (parts per billion by volume)
5/28/86 Camio Station, South Mangum Street, Durham, NC INDOORS	
Benzene	§0.5
5/29/86 Camio Station OUTDOORS IN YARD	
Toluene	3 3 ND ND ND ND ND ND ND ND ND
1,1,1-Trichloroethane	ND ND ND ND ND ND ND 200 ND ND ND
6/2/86 Room S-256, EPA Annex, T. W. Alexander Drive, RTP, NC INDOOR LABORATORY AIR	
Trichloroethylene	4 2 1 2 1
Toluene	ND 4 10 3 3
6/3/86 Jenkins Road, 1 mile south of NC54, RTP, NC OUTDOORS, SAMPLER IN CAR	
Benzene	5 ND
Trichloroethylene	ND 3
6/4/86 133 Montclair Circle, Durham, NC OUTDOORS IN DRIVEWAY, SAMPLER IN CAR	
Benzene	4
Northgate Mall Parking Garage, Durham, NC OUTDOORS UNDER ROOF, SAMPLER IN CAR	
Benzene	4 ND ND ND ND
Toluene	ND 2 4 ND ND
6/5/86 Corner of Reservoir and Bowen Streets, Durham, NC OUTDOORS ACROSS FREEWAY FROM SOUTHCHEM PLANT, SAMPLER IN CAR	
1,1,1-Trichloroethane	3355 ND ND
Trichloroethylene	1 ND ND
Benzene	ND 17 ND
Umstead Park, Raleigh, NC OUTDOORS IN BOATHOUSE PARKING LOT, SAMPLER IN CAR	
Benzene	7 ND ND ND ND ND

ND = not detected



Event		on	off
1	pump	0	10
2	cal gas	8	9
3	v2 & v3	10	200
4	v1 & v4	10	11
5	v5	11	200

Figure 6. Standard configuration of Photovac 10S50 with packed column.

backflush configuration shown in Figure 6 should be compared with the capillary column installation in Figure 7. The valves are all shown in their non-energized positions. When automatic injection was attempted, higher column head pressures caused carrier gas to flow into the sample loop at both ends for more than one second after it was switched into the carrier stream, and at least 15 seconds were required to sweep the sample completely out of it. No significant improvement in resolution was gained from using the capillary column instead of the packed column because of the large dead volume of the loop, which consisted of a 17 centimeter length of Teflon tubing of 2.74 millimeters inside diameter. When it was replaced with a 1.74 meter length of tubing with 0.81 millimeter inside diameter which had the same volume (1 milliliter) a small improvement in resolution became apparent.

The plumbing was rearranged to place the loop normally in the carrier stream and only out of it during sampling (Figure 8). This was done to improve efficiency of operation, provide a constant flow of carrier through the sample loop except during sampling, and avoid the issue of how much time was actually required to sweep out the sample loop. This flow path resulted in slightly lower responses to calibrant. One reason could have been that the loop was chronically contaminated with calibrant during operation in the other configuration. Consecutive injections of NBS SRM No. 1805 were made to test this (Table V).

TABLE 5. SHORT TERM RESPONSE STABILITY (a)

Time of Day	Response (b) (volt*second)
0825	390
0843	375
0855	350
0956	345
1252	340
1316	355
1344	350
1439	345
1456	350
1512	350
1529	345

a. To consecutive injections of NMS SRM No. 1805 (0.254 parts per million benzene in nitrogen).

b. Converted to absolute response (at gain 1000) by multiplying by (1000/gain).

By the third injection, response had fallen to about 350 volt*second and stabilized. These results suggest low level benzene contamination of the sample loop at the beginning of the series of injections. They also suggest

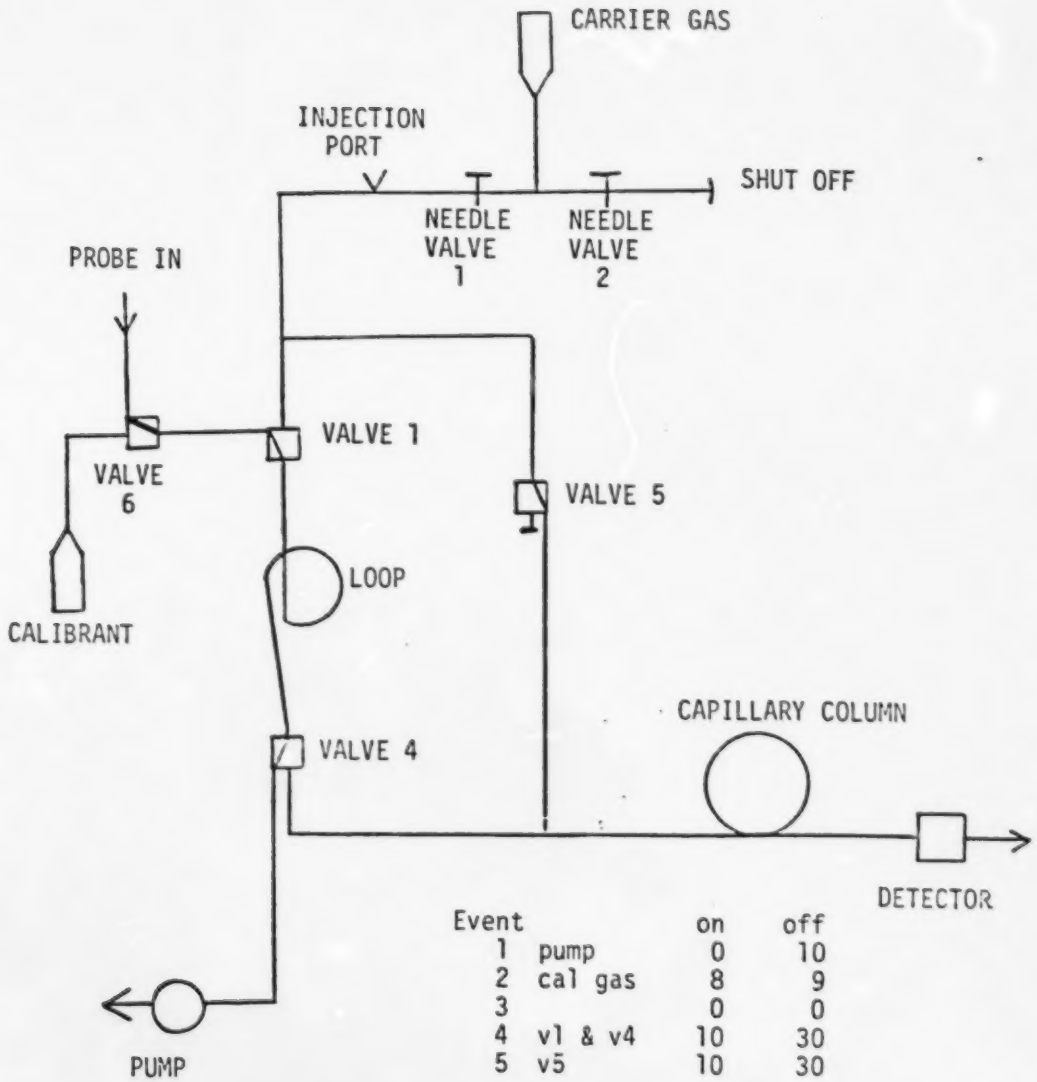
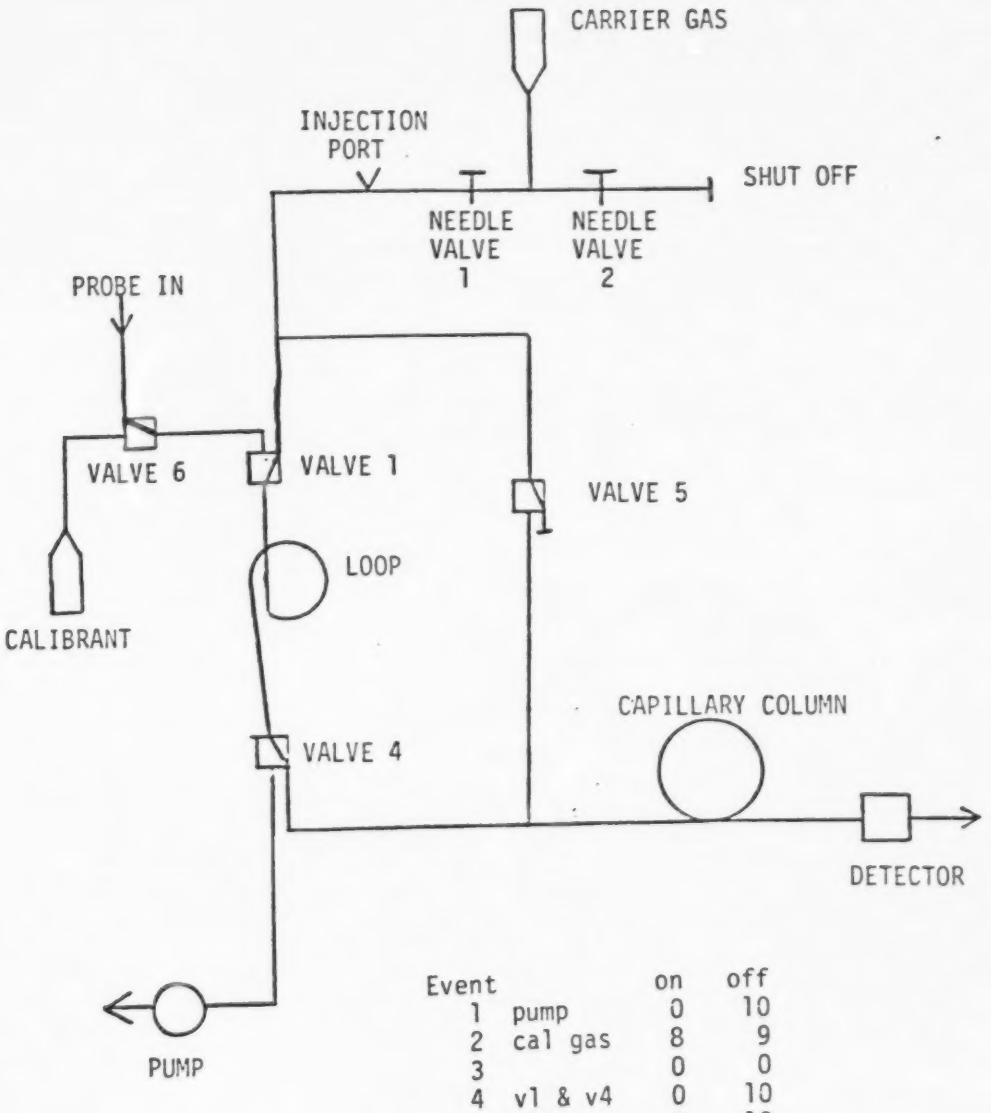


Figure 7. Photovac 10S50 with capillary column installed. No backflush. Sample loop normally not in line with carrier flow.



Event		on	off
1	pump	0	10
2	cal gas	8	9
3		0	0
4	v1 & v4	0	10
5	v5	0	10

Figure 8. Photovac 10S50 with capillary column installed. No backflush. Sample loop normally in line with carrier flow.

that short term stability of the detector is extremely good and that the quality of results obtained between periodic recalibrations during the course of a day would be unlikely to suffer from variation in detector sensitivity.

Library No. 4 was calibrated for 13 compounds at a carrier flow rate of 40 milliliters per minute. Tetrachloromethane was not seen at this flow rate even with repeated, separate injections. Retention times at 40 milliliters per minute are listed in Table VI. Library No. 3 was calibrated for 9 compounds (all of which eluted before 1,2-dibromoethane) at a carrier flow rate of 20 milliliters per minute, and tetrachloromethane was seen at this flow rate. The calibration mixtures used are summarized in Table VI. The different concentrations reflect the relative sensitivity of the photoionization detector to each compound. These calibrations were tested five days later by preparing fresh calibration mixtures and analyzing them. Results for library 3 are shown in Table VII. The concentrations in the new calibration mixture are listed in the first column. The initial responses based on previous calibration data are listed in the second column of the table. Since toluene fell outside the library retention window, it was missed. The third column shows the same data after being recalibrated by specifying that the missed peak was toluene at a concentration of 0.277 parts per million by volume. The uncorrected data were erroneous, but not unreasonably so. Because five days had elapsed, and because the temperature was different, changes in both retention times and response factors were expected. After recalibration, the results were in reasonable agreement with expected values. The discrepancies were probably due mostly to the uncertainty of standards prepared by static dilution of headspace vapors.

Results for library 4 were shown in Table VIII. Again, the calibrant peak (bromobenzene) and five others were missed before recalibration. In this case the retention time of bromobenzene was recalibrated but not its concentration. After recalibration all compounds were properly identified, and most of their concentrations were in rough agreement with expected values, even though the calibrant concentration had not been corrected. Again, in view of the use of standards prepared by static dilution of headspace vapors, the results were reasonable. The three halocarbon compounds at the bottoms of Tables VII and VIII were run separately, immediately after recalibration. This was done because they were not resolved chromatographically from the other compounds on the fused silica capillary column. Tetrachloromethane was not resolved on the capillary column from benzene even at 20 milliliters per minute. Neither was dichloromethane separated from 1,1-dichloroethylene or 1,2-dichloroethane from 1,1,1-trichloroethane. At a carrier flow of 10 milliliters per minute these compounds were partially resolved, but only at very low concentrations. Further improvement in resolution is desirable.

Intermittent failure of the printer-plotter necessitated return of the unit to Photovac for repair prior to evaluation of peak resolution factors or field testing with the capiliary column.

TABLE 6. CALIBRATION WITH CAPILLARY COLUMN (a)

Compound	Retention time at 40 ml/min (seconds)	Concentration (parts per million)
Dichloromethane	38.9	6.46
Trichloromethane	61.7	36.2
1,1,1-Trichloroethane	153.3	13.7
Benzene	173.8	0.323
Trichloroethylene	242.6	0.250
Toluene	443.1	0.277
1,2-Dibromoethane (b)	546.4	0.463
Tetrachloroethylene (b)	664.5	0.377
Chlorobenzene (b)	867.4	0.771
o-Xylene (b)	1385.8	1.12
Bromobenzene (b)	1795.6	0.724
1,1-Dichloroethylene (c)	59.2	0.949
1,2-Dichloroethane (c)	144.0	15.2
Tetrachloromethane (c)	(d)	20.3

a. 0.53 millimeter X 25 meter fused silica with chemically bonded methyl silicone stationary phase.

b. Not used in Calibrating library 3.

c. Calibrated separately because they were not resolved from the other compounds.

d. Not seen at 40 milliliters per minute.

TABLE 7. CALIBRATION STABILITY AT 20 MILLILITERS PER MINUTE (a)

Compound	Concentrations (parts per million) Expected (b)	Found before Recalibration (c)	Found after Recalibration (d)
Dichloromethane	4.45	1.66	2.93
Trichloromethane	33.1	16.0	28.1
1,1,1-Trichloroethane	12.5	10.8	19.0
Benzene	0.323	0.143	0.251
Trichloroethylene	0.250	0.324	0.569
Toluene	0.277	missed	0.277
1,1-Dichloroethylene	0.684	(e)	0.721
1,2-Dichloroethane	14.5	(e)	11.8
Tetrachloromethane	19.4	(e)	18.1

a. 0.53 millimeter X 25 meter fused silica with chemically bonded methyl silicone stationary phase.

b. Concentrations in the standard mixture were prepared by static dilution of headspace vapors.

c. Concentrations were reported without recalibration based on calibrations done 5 days before.

d. Concentrations were reported after the calibration had been corrected by identifying the toluene peak and assigning the correct concentration to it.

e. The two chloroethylenes and tetrachloromethane were run separately after correcting calibration because they were not chromatographically resolved from the other compounds.

TABLE 8. CALIBRATION STABILITY AT 40 MILLILITERS PER MINUTE (a)

Compound	Concentrations (parts per million) Expected (b)	Found before Recalibration (c)	Found after Recalibration (d)
Dichloromethane	4.45	7.58	7.58
Trichloromethane	33.1	24.3	24.3
1,1,1-Trichloroethane	12.5	21.6	21.6
Benzene	0.323	0.310	0.310
Trichloroethylene	0.250	0.355	0.355
Toluene	0.277	missed	0.316
1,2-Dibromoethane	0.488	missed	0.530
Tetrachloroethylene	0.397	missed	0.438
Chlorobenzene	0.814	missed	1.80
o-Xylene	1.19	missed	1.75
Bromobenzene	0.767	missed	0.791
1,1-Dichloroethylene	0.684	(e)	1.04
1,2-Dichloroethane	14.5	(e)	18.3
Tetrachloromethane	13.4	(e)	not seen

a. 0.53 millimeter X 25 meter fused silica with chemically bonded methyl silicone stationary phase.

b. Concentrations in the standard mixture were prepared by static dilution of headspace vapors.

c. Concentrations were reported without recalibration based on calibrations done 5 days before.

d. Concentrations were reported after the calibration was corrected by identifying the bromobenzene peak without assigning a corrected concentration to it.

e. The two chloroethylenes and tetrachloromethane were run separately after correcting calibration because they were not chromatographically resolved from the other compounds.

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APPENDIX A

Listings follow of data acquisition and data processing programs for a Hewlett-Packard Model 85 computer equipped with a Model 6942A multiprogrammer interface. They are shown as subprograms but can be run independently by making appropriate modifications to the first and last statements. "PVSCQU" was the data acquisition program, and "PVLRREV" was the data processing program.

```
10 SUB "PVSCOU"
20 ! DATA AQUISITION PROGRAM FOR PHOTOVAC 10S50. ADAPTED Mar 86 by REB
30 ! FLAG(1):  READ FILE, NOT PHOTOVAC
40 ! FLAG(2):  CALIBRATION RUN
50 OPTION BASE 1@ CRT IS 1 @ PRINTER IS 2 @ PLOTTER IS 1
60 SHORT A(4000),B(80)
70 DIM D$[30],T$[30],A1$[600],A2$[30]
80 SARRAY A1$
90 DIM C(20)
100 INTEGER A,A1,B,B1,I,J,N,N1
110 D$=DATE$
120 ON KEY# 1,"STOP" GOTO 570
130 GOTO 160
140 BEEP @ DISP "QUIT?" @ INPUT Q$@ IF Q$="Y" THEN 1470
150 IF Q$#"N" THEN 140
160 CLEAR @ BEEP @ DISP "READ FILE(F) OR RUN PHOTOVAC(P)?" @ INPUT Q$
170 IF Q$="P" THEN CFLAG 1 @ GOTO 210
180 IF Q$#"F" THEN 140
190 SFLAG 1
200 GOSUB 1210 @ GOTO 140
210 BEEP @ DISP "IS THIS A CALIBRATION?" @ INPUT Q$@ IF Q$="N" THEN CFLAG 2
@ GOTO 240
220 IF Q$#"Y" THEN 210
230 SFLAG 2
240 N1=1
250 IF N1>20 THEN N1=20 @ BEEP @ CLEAR @ GOTO 320
260 CLEAR @ BEEP @ DISP "ENTER COMPOUND NAME" @ DISP "Enter STOP when done."
270 INPUT A$@ SLET A1$(N1) = A$
280 IF A$="STOP" THEN N1=N1-1 @ GOTO 320
290 IF FLAG(2) THEN BEEP @ DISP "ENTER ng/microliter" @ INPUT C(N1)@ GOTO 31
0
300 C(N1)=1
310 N1=N1+1 @ GOTO 250
320 DISP "ENTER CHROMATOGRAM FILENAME" @ INPUT F$
330 DISP "ENTER TIME DELAY IN MINUTES"
340 DISP "D1=" @ INPUT D1@ D1=D1*60000
350 DISP "D2=" @ INPUT D2@ D2=D2*60000
360 DISP "D3=" @ INPUT D3@ D3=D3*60000
370 DISP "D4=" @ INPUT D4@ D4=D4*60000
380 BEEP @ CLEAR @ REDIM A(4000)
390 DISP "GAIN" @ INPUT G9
400 G9=1000/G9
410 M1=10 @ A9=10
420 DISP "MICROLITERS" @ INPUT V9
430 DISP "PRESS CONT TO START" @ PAUSE
440 T1$=TIME$
450 CLEAR @ CLEAR 723
460 OUTPUT 723 ;"SF,4,3.1,.05,12T"
470 J=1 @ I=1 @ N=4000
480 IF J>N THEN 570
490 GOSUB 690 @ BEEP
500 WAIT D1 @ D1=D2 @ D2=D3 @ D3=D4
510 IF I=J+1000 THEN J=I @ GOTO 480
520 OUTPUT 723 ;"OP,6,1T IP,4T"
530 SEND 7 ; UNL MLA TALK 23 SCG 1
540 ENTER 7 USING "#,K" ; A(I)@ PENUP @ PLOT I,A(I)
550 WAIT 50
560 I=I+1 @ GOTO 510
570 N=I-1 @ J=1 @ I=1 @ REDIM A(N)
580 BEEP @ DISP "INTEGRATE A PEAK?" @ INPUT Q$@ IF Q$="N" THEN 610
590 IF Q$#"Y" THEN 580
```

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```
600 GOSUB 710
610 IF FLAG(1) THEN 140
620 BEEP @ DISP "FINISHED WITH CHROMATOGRAM " @ DISP F$;"?" @ INPUT Q$@ IF Q
$="N" THEN 580
630 IF Q$≠"Y" THEN 620
640 BEEP @ DISP "ARE YOU SURE?" @ INPUT Q$@ IF Q$="N" THEN 580
650 IF Q$≠"Y" THEN 640
660 DISP "ANOTHER INJECTION," @ DISP "SAME SERIES?" @ INPUT Q$@ IF Q$="Y" TH
EN 320
670 IF Q$="N" THEN 140
680 GOTO 660
690 GCLEAR @ SCALE I,I+1000,-(.1*M1),M1 ! SCALE PEAK SUBROUTINE
700 PENUP @ MOVE 0,0 @ RETURN
710 A=1 @ B=N ! DISPLAY AND INTEGRATE PEAK SUBROUTINE
720 BEEP @ DISP "ENTER PEAK FILENAME" @ INPUT N$
730 BEEP @ DISP "ENTER COMPOUND NAME" @ INPUT T$
740 FOR I=1 TO N1 @ A2$=GET$(A1$(I))
750 IF T$=A2$ THEN C1=C(I) @ GOTO 770
760 NEXT I
770 CLEAR @ GCLEAR @ BEEP @ DISP "DISPLAY PEAK" @ DISP "BASELINE POINTS? (LO
W, HIGH)"
780 DISP A,B
790 INPUT A,B
800 BEEP @ DISP "VERTICAL SCALE" @ DISP M1 @ INPUT M1
810 B9=INF
820 FOR I=A-41 TO B+40 @ IF B9>A(I) THEN B9=A(I)
830 NEXT I
840 GCLEAR @ SCALE A-41,B+40,-(.05*M1),M1 @ PENUP @ MOVE A-41,0
850 FOR I=A-41 TO B+40 @ PENUP @ PLOT I,A(I)-B9 @ NEXT I
860 MOVE A,0 @ IDRAW 0,.2*M1 @ PENUP @ IMOVE 0,.05*M1 @ LDIR 90 @ LABEL A @
PENUP
870 MOVE B,0 @ IDRAW 0,.2*M1 @ PENUP @ IMOVE 0,.05*M1 @ LABEL B @ PENUP @ LD
IR 0
880 MOVE A,A(A)-B9 @ DRAW B,A(B)-B9 @ PENUP
890 MOVE A,.95*M1 @ LDIR 0 @ LABEL "VERTICAL SCALE ";M1
900 BEEP @ PAUSE
910 BEEP @ DISP "REPLOT?(Y/N)"
920 INPUT Q$
930 IF Q$="Y" THEN 770
940 IF Q$≠"N" THEN 910
950 BEEP @ DISP "INTEGRATE? (Y/N)"
960 INPUT Q$@ IF Q$="N" THEN 990
970 IF Q$≠"Y" THEN 950
980 GOSUB 1000
990 RETURN
1000 A1=A-41 @ B1=B-40 @ D=0 @ E=0 @ T1=0 @ U=0 ! INTEGRATION SUBROUTINE
1010 FOR I=1 TO 40 @ B(I)=A(I+A1)*G9/A9 @ NEXT I
1020 FOR I=41 TO 80 @ B(I)=A(I+B1)*G9/A9 @ NEXT I
1030 FOR I=1 TO 80 @ D=D+B(I) @ E=E+B(I)^2 @ NEXT I @ D=D/80
1040 S=SQR((E-80*D^2)/79)
1050 A5=A(A) @ B5=A(B)
1060 FOR I=A TO B
1070 A6=A(I)-A5-(I-A)*(B5-A5)/(B-A) @ A6=A6*G9/A9
1080 IF A6>U THEN U=A6
1090 T1=T1+A6
1100 NEXT I @ T1=T1*.183978
1110 GOSUB 1260
1120 BEEP @ DISP "PRINT PEAK? (Y/N)"
1130 INPUT Q$@ IF Q$="N" THEN 1160
1140 IF Q$≠"Y" THEN 1120
1150 GRAPH @ COPY @ PRINT @ PRINT @ PRINT @ PRINT
```


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```
1160 BEEP @ DISP "STORE FILE ";N$;"?" @ INPUT Q$@ IF Q$="N" THEN 1200
1170 IF Q$#"Y" THEN 1160
1180 CREATE N$&"2:D701",1,134 @ ASSIGN# 2 TO N$&"2:D701"
1190 PRINT# 2 ; D$,T$,U,T1,V9,C1,S,A,B,D @ ASSIGN# 2 TO *
1200 RETURN
1210 DISP "ENTER FILENAME" @ INPUT N$ ! READ PEAK SUBROUTINE
1220 CRT OFF @ ASSIGN# 2 TO N$&"2:D701"
1230 READ# 2 ; D$,T$,U,T1,V9,C1,S,A,B,D@ ASSIGN# 2 TO * @ CRT ON
1240 GOSUB 1260
1250 RETURN
1260 PRINT D$ ! PRINT RESULTS SUBROUTINE
1270 IF FLAG(1)=0 THEN PRINT T1$
1280 PRINT F$ @ PRINT N$
1290 PRINT T$
1300 PRINT V9;" microliters"
1310 PRINT "PEAK HEIGHT        PEAK AREA"
1320 PRINT USING 1340 ; U,T1
1330 PRINT "     VOLTS         VOLT*SEC" @ PRINT
1340 IMAGE 4DZ.4D,4X,4DZ.4D
1350 IMAGE 6DZ.8D," nanograms"
1360 IMAGE 6DZ.8D," microliters"
1370 IF FLAG(2) THEN PRINT USING 1350 ; C1*V9 @ GOTO 1390
1380 PRINT USING 1360 ; V9
1390 PRINT USING 1400 ; S
1400 IMAGE "SDEV= ",DZ.4D
1410 IMAGE "BASELINE= ",2DZ.6D
1420 PRINT USING 1410 : D
1430 PRINT USING 1440 ; A,B
1440 IMAGE "FROM ",4D," TO ",4D
1450 PRINT @ PRINT
1460 RETURN
1470 CLEAR @ SUBEND
```

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```
10 SUB "PVLRREV"
20 ! LINEAR REGRESSION OF PHOTOVAC 10A10 CALIBRATION DATA, WRITTEN June 85 b
y reb
30 PLOTTER IS 1 @ CRT IS 1 @ PRINTER IS 2
40 OPTION BASE 1
50 DIM D$[30],T$[30],N1$[30]
60 SHORT P,V9,S(20),Y(20),U(20),S1(20),X(20)
70 INTEGER I,N,I1
80 DIM N$[30],A1$[200]
90 SARRAY A1$
100 CLEAR
110 DISP "ENTER NAME OF COMPOUND" @ INPUT N1$
120 N=1 @ A$=""
130 IF N>20 THEN N=20 @ BEEP @ CLEAR @ GOTO 190
140 CLEAR @ DISP A$ @ DISP "ENTER FILENAME ";N
150 DISP "Enter STOP when done."
160 INPUT A$@ SLET A1$(N) = A$
170 IF A$="STOP" THEN N=N-1 @ GOTO 190
180 N=N+1 @ GOTO 130
190 CRT OFF @ FOR I1=1 TO N
200 N$=GET$(A1$(I1))
210 ASSIGN# 2 TO N$&"2:D701"
220 READ# 2 ; D$,T$,U,T1,V9,C1,S,A,B1,D
230 ASSIGN# 2 TO *
240 IF T$#N1$ THEN BEEP @ DISP "FILE ";N$;" DOES NOT BELONG." @ PAUSE
250 Y(I1)=T1 @ U(I1)=U @ S(I1)=V9*C1 @ S1(I1)=S
260 GOSUB 740
270 NEXT I1 @ CRT ON
280 IF N<3 THEN 1050 ! >2 POINTS NEEDED FOR REGRESSION
290 ! LINEAR REGRESSION, AREA & HEIGHT
300 Z=0 @ X1=0 @ Y1=0 @ Z1=0 @ P=0 @ Q=0 @ X2=0 @ Y2=0 @ Z2=0 @ W=0 @ W1=0
310 FOR I=1 TO N
320 IF Z<S(I) THEN Z=S(I)
330 IF W<Y(I) THEN W=Y(I)
340 IF W1<U(I) THEN W1=U(I)
350 X1=X1+S(I)
360 Y1=Y1+Y(I)
370 Z1=Z1+U(I)
380 P=P+S(I)*Y(I)
390 Q=Q+U(I)*Y(I)
400 X2=X2+S(I)^2
410 Y2=Y2+Y(I)^2
420 Z2=Z2+U(I)^2
430 NEXT I @ CLEAR
440 M=(X1*Y1/N-P)/(X1^2/N-X2)
450 M2=(Z1*Y1/N-Q)/(Z1^2/N-Z2)
460 X=X1/N @ Y=Y1/N @ Z4=Z1/N
470 B=Y-M*X @ B2=Y-M2*Z4
480 V=X2/N-X1^2/N^2 @ V3=Z2/N-Z1^2/N^2
490 V1=Y2/N-Y1^2/N^2
500 R1=M*SQR(V)/SQR(V1) @ R2=M2*SQR(V3)/SQR(V1)
510 ! CALCULATE SDEV OF BACKGROUND
520 S=0
530 FOR I=1 TO N
540 S1(I)=S1(I)^2
550 NEXT I
560 FOR I=1 TO N
570 S=S+S1(I)
580 NEXT I
590 S=SQR(S/N)
600 ! CALCULATE DETECTION LIMITS
```

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```
610 L=2000*S/M
620 PRINT USING 630 ! PRINT RESULTS
630 IMAGE //"LINEAR REGRESSION"//
640 IMAGE /"SLOPE",4X,DZ.4DE," V*sec/ng"/"INTERCEPT ",DZ.4DE," V*sec"/"CORR
COEF ",MZ.6D,//
650 PRINT USING 640 ; M;B;R1
660 IMAGE "STANDARD DEVIATION = "/4DZ.4D
670 PRINT USING 660 ; S
680 IMAGE /"Detection Limit ="/4DZ.9D,/" picograms"
690 PRINT USING 680 ; L
700 F1=Z @ L$="V*sec" @ B5=B @ M5=M
710 FOR I=1 TO N @ X(I)=S(I) @ NEXT I
720 GOSUB 880
730 COPY @ CLEAR @ GOTO 1060
740 PRINT N$ ! PRINT INDIVIDUAL PEAK DATA SUBROUTINE
750 PRINT D$
760 PRINT T$
770 PRINT V9;" microliters"
780 PRINT "PEAK HEIGHT   PEAK AREA"
790 PRINT USING 810 ; U(I1),Y(I1)
800 PRINT "      VOLTS          VOLT*SEC"
810 IMAGE 4DZ.4D,4X,4DZ.4D
820 PRINT S(I1);" nanograms"
830 PRINT USING 840 ; S1(I1)
840 IMAGE "SDEV= ",DZ.4D
850 PRINT USING 860 ; A,B1
860 IMAGE "FROM ".4D," TO ",4D///
870 RETURN
880 GCLEAR @ PRINT @ SCALE -(F1/10),1.2*F1,-(W/10),1.1*W ! PLOT SUBROUTINE
890 F2=1/10^IP(LGT(F1)-2) @ G2=1/10^IP(LGT(W)-2)
900 F3=IP(F1*F2*1.05)/F2 @ G3=IP(W*G2*1.05)/G2
910 XAXIS 0,.5*F3,0,F3
920 YAXIS 0,.5*G3,0,G3
930 FOR I=1 TO N
940 MOVE X(I),Y(I)
950 IMOVE 0,.012*W @ IDRAW 0,-(.024*W) @ IMOVE .00975*F1,.012*W @ IDRAW -(.0
195*F1),0
960 NEXT I
970 MOVE F1/10,G3
980 LABEL VAL$(G3)
990 LDIR 90 @ MOVE -(F1/100),W/10 @ LABEL L$ @ MOVE F3,W/10 @ LABEL VAL$(F3)
 @ LDIR 0
1000 MOVE .8*F3,-(W/10) @ LABEL "nanograms"
1010 PLOT 0,B5
1020 PLOT F1,M5*F1+B5
1030 RETURN
1040 ! N<3 ESCAPE DUMP
1050 PRINT "Three or more points are" @ PRINT "required for linear regressio
n."
1060 PRINT @ PRINT @ PRINT @ PRINT
1070 BEEP @ DISP "DO ANOTHER COMPOUND?" @ INPUT Q$@ IF Q$="Y" THEN 100
1080 IF Q$<>"N" THEN 1070
1090 PRINT @ PRINT @ PRINT @ PRINT @ PRINT @ PRINT @ PRINT @ CLEAR @ SUBEND
```

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